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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE CUPROSAMMONIUM BROMIDES AND THE
CUPRAMMONIUM SULPHOCYANATES.

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• WITH regard to the possible compounds of cuprosammonium our knowledge is by no means complete. Many compounds which we should expect to find are not mentioned in chemical literature, and many which have been found are very imperfectly described. The present paper records the results of an investigation which had as its aim the filling up of some of the gaps in this direction; in particular we hoped to discover *cuprosammonium* double salts of the type $\text{Cu}_2(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$, analogous to the *cupriammonium* compounds which have recently been investigated here. While this latter hope has not yet found its fulfilment in fact, we have succeeded in preparing four new simple *cuprosammonium* compounds:—

- (1) $\text{Cu}_2(\text{NH}_3)_2\text{Br}_2$,
- (2) $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$,
- (3) $\text{Cu}_2(\text{NH}_3)_6\text{Br}_2$,
- (4) $\text{Cu}_2(\text{NH}_3)_{5(?)}\text{(SCN)}_2$;

and one *cupriammonium* sulphocyanate:—

- (5) $\text{Cu}(\text{NH}_3)_4(\text{SCN})_2$.

1. CUPROSAMMONIUM BROMIDE, $\text{Cu}_2\text{Br}_2 \cdot 2 \text{NH}_3$.

To prepare this compound, about ten grams of precipitated cuprous bromide were dissolved in the least possible amount of ammoniac hydrate solution, and about twenty-five cubic centimeters of acetic acid were added. All operations were carried on with the help of a complex apparatus in an atmosphere of hydrogen, and the solution was evaporated spontaneously over sulphuric acid in a bell jar filled with hydrogen. After a day or two the bromide crystallized out in long colorless crystals.

Some difficulty was experienced in obtaining the substance dry in a pure state, as it begins to oxidize with the greatest readiness immediately upon removal from the mother liquor. The best results were obtained by the following method. The bell jar was so arranged that the mother liquor could be siphoned off, and successive portions of alcohol and ether could be introduced, the crystals all the time remaining in an atmosphere of hydrogen. After thus washing with alcohol and ether, some of the hydrogen was pumped out, and the last drops of ether evaporated in the partial vacuum. Prepared in this way, the substance was obtained in perfectly colorless long flat prisms. When thoroughly dry, it is stable and permanent at ordinary temperatures in the air. It is of course readily soluble in ammoniac hydrate and in nitric acid, but deposits cuprous bromide upon treatment with other mineral acids, or with acetic acid. On exposure to moist air, and when placed in water, the substance oxidizes in a manner somewhat peculiar. The crystals first take on a bluish green tint, then gradually turn to a bright yellow, and finally change to a copper-red color. Owing to the fact that this change takes place only on the surface, the crystal within being unchanged, it was impossible to ascertain the nature of the yellow coating.

Cuprosammonium bromide was repeatedly obtained under a great variety of circumstances during many fruitless attempts to make the double salt $\text{Cu}_2(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$. Between -10° and 25° the simple bromide appears to be by far the least soluble of the possible compounds obtainable from mixtures of cuprous copper, ammonia, bromine, and acetic acid.

In the analyses the bromine was determined as argentic bromide after dissolving the substance in ammoniac hydrate, allowing the copper to oxidize by exposure to the air, and acidifying with nitric acid. Copper was determined electrolytically in a new portion after evaporating with nitric and sulphuric acids. The ammonia was distilled over potash.

Analyses of $\text{Cu}_2\text{Br}_2 \cdot 2 \text{NH}_3$.

- I. 0.2459 gram of substance gave, on electrolyzing, 0.0963 gram of copper.
- II. 0.2059 gram of substance, distilled with caustic potash, required 13.04 cubic centimeters of decinormal acid solution for neutralization.
- III. 0.3537 gram of substance, distilled with caustic potash, required 22.00 cubic centimeters of decinormal acid solution for neutralization.

IV. 0.3191 gram of substance yielded 0.3732 gram of argentic bromide.

V. 0.3045 gram of substance yielded 0.3576 gram of argentic bromide.

	Calculated for $\text{Cu}_2\text{Br}_2 \cdot 2 \text{NH}_3$.	Found.					
		I.	II.	III.	IV.	V.	Average.
Copper . . .	39.59	39.24	...	...	...	...	39.24
Ammonia . . .	10.63	...	10.78	10.61	...	...	10.69
Bromine . . .	49.78	...	...	...	49.78	49.97	49.88
	100.00						99.81

2. CUPROSAMMONIUM SULPHOCYANATE, $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$.

In the first place, cuprous hydrate was prepared by adding an excess of a solution of sodic hydrate to cuprous chloride. The precipitated hydrate was washed once or twice and dissolved in the least possible amount of ammoniac hydrate solution. On the addition of a concentrated solution of ammoniac sulphocyanate, cuprosammonium sulphocyanate is precipitated as a white crystalline powder. Attempts to obtain larger crystals by using more dilute solutions were unsuccessful. The substance was washed with alcohol and ether, and dried rapidly by pressing between filter paper. Owing to the finely divided state in which the substance comes down, it is very difficult to dry it thoroughly and quickly in this fashion. It cannot be dried by exposure to the air, or over sulphuric acid, on account of the readiness with which it loses ammonia. Hence the analytical results are somewhat low on account of the presence of traces of moisture. The only remarkable property of this compound is its instability. Most of the other compounds of copper containing two molecules of ammonia are extremely stable, some of them retaining all their ammonia even at 100° . The cuprosammonium sulphocyanate, however, loses ammonia rapidly even at ordinary temperatures.

In many samples which had been allowed to stand for some time, the sulphocyanic acid also was found to be deficient. The two analyses given below are those of the two freshest preparations, and even they leave much to be desired in the way of accuracy. It is possible that the molecular rearrangement caused by the loss of the ammonia may induce an especial tendency toward oxidation, which, combined with

the instability of cupric sulphocyanate,* might set free or decompose some sulphocyanic acid. Although, as has been said, the analyses are not exact, they are quite sufficiently accurate to prove the formula $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$, for the respective atomic ratios found are 1.01 : 1.00 : 1.00, instead of the theoretical 1 : 1 : 1.

In the analysis the sulphocyanic acid was determined volumetrically according to the method of Volhard, after dissolving the substance in ammoniac hydrate and allowing the copper to oxidize by exposure to the air.

Analyses of $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$.

- I. 0.2504 gram of substance gave, on electrolysis, 0.1133 gram of copper.
- II. 0.2297 gram of substance required 16.09 cubic centimeters of a decinormal solution of silver nitrate for precipitation of the sulphocyanic acid.
- III. 0.2645 gram of substance required 18.60 cubic centimeters of a decinormal solution of argentic nitrate for precipitation of the sulphocyanic acid.
- IV. 0.2390 gram of substance required, after distilling with caustic potash, 16.57 cubic centimeters of a decinormal acid solution for neutralization.
- V. 0.2822 gram of substance, after distilling with caustic potash, required 19.84 cubic centimeters of a decinormal acid solution for neutralization.

	Calculated for $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$.	Found.					
		I.	II.	III.	IV.	V.	Average.
Copper . . .	45.83	45.25	...	...	...	...	45.25
Ammonia . . .	12.29	...	...	...	11.83	12.00	11.91
Sulphocyanic acid	41.88	...	40.70	40.86	...	...	40.78
	100.00						97.94

Atomic ratios of copper to ammonia and to sulphocyanic acid found = 1.01 : 1.00 : 1.00.

* Graham Otto, Michaelis, III. 892.

3. TETRAMMON-CUPROSAMMONIUM BROMIDE, $\text{Cu}_2\text{Br}_2(\text{NH}_3)_6$?

This compound is prepared by placing dry, finely powdered cuprous bromide in a bulb tube which is packed in ice, and passing in dry ammonia gas until the mass is saturated. The ammonia is absorbed with evolution of heat, the white cuprous bromide meanwhile turning dark brown and becoming hard and lumpy. In order to insure saturation, the mass must be removed from the tube occasionally and powdered. The saturated compound is a black powder, decomposed by water, soluble in ammoniac hydrate and nitric acid. It is excessively unstable, giving off ammonia with the greatest ease. On this account the substance must be weighed while ice-cold, and hence also its analysis is far from satisfactory. The copper was determined in the residue from the ammonia determinations, in order to be sure of the proportion of copper to ammonia. The atomic proportions obtained in this way show that the formula given above is probably correct, although the analyses cannot be considered sufficiently definite to furnish conclusive proof. It is certain that the compound contains *at least* six molecules of ammonia.

Analyses of $\text{Cu}_2\text{Br}_2(\text{NH}_3)_6$.

- I. 0.3276 gram of substance, distilled with caustic potash, required 50.30 cubic centimeters of a decinormal acid solution for neutralization.
- II. 0.5746 gram of substance, distilled with caustic potash, required 87.03 cubic centimeters of a decinormal acid solution for neutralization.
- III. 0.3276 gram of substance, — residue from I., — gave on electrolysis 0.1027 gram of copper.

	Calculated for $\text{Cu}_2\text{Br}_2 \cdot 6 \text{NH}_3$.	I.	II.	Found.	III.	Average.
Copper	32.66				31.38	31.38
Ammonia	26.29	26.20	25.84			26.02

Atomic ratio of copper to ammonia found = 1 : 3.10.

4. TRIAMMON-CUPROSAMMONIUM SULPHOCYANATE, $\text{Cu}_2(\text{NH}_3)_5(\text{SCN})_2$.

This substance is prepared by a method similar to that used in the preparation of the saturated bromine compound described above. Dry ammonia gas is passed over dry powdered cuprous sulphocyanate, until the solid is saturated, the cuprous sulphocyanate being cooled by ice. The substance is a black powder, and possesses no remarkable properties.

It is very unstable, giving up ammonia rapidly on exposure to the air. The simplest method of determining the composition of the substance would naturally be to start with a known weight of cuprous sulphocyanate, pass in ammonia until saturated, and weigh again in sealed tube, no further analysis being necessary. This method is impossible, however, since, as in the case of the saturated bromine compound, the cuprous sulphocyanate hardens in absorbing the ammonia and has to be removed from the tube occasionally and powdered in order to insure saturation. As in the case of the bromine compound, too, the results of the analysis are unsatisfactory on account of the extreme instability of the compound. Copper was determined in the same sample with the ammonia in order to be sure of the proportion of copper to ammonia, and from the proportions so obtained it seems probable that the formula given is correct, in spite of the low results of the analyses. In any event, the atomic ratios $\text{Cu}_2 : (\text{NH}_3)_5$ must be assumed to represent the *minimum* amount of ammonia present in this compound.

Analyses of $\text{Cu}_2(\text{SCN})_2(\text{NH}_3)_5$.

- I. 0.5633 gram of substance, distilled with caustic potash, required 83.40 cubic centimeters of a decinormal acid solution for neutralization.
- II. 0.4176 gram of substance, distilled with caustic potash, required 57.90 cubic centimeters of a decinormal acid solution for neutralization.
- III. 0.4176 gram of substance gave, on electrolyzing, 0.1571 gram of copper.

	Calculated for $\text{Cu}_2(\text{SCN})_2, 5 \text{ NH}_3$.	I.	II.	Found.	III.	Average.
Copper	38.81				37.62	37.62
Ammonia	25.97	25.27	23.66			24.47

Atomic ratio of copper to ammonia found = 2 : 5.05.

5. DIAMMON-CUPRIAMMONIUM SULPHOCYANATE, $\text{Cu}(\text{SCN})_2(\text{NH}_3)_4$.

In addition to the cuprosammonium compounds just described, we succeeded in preparing a new *cupriammonium* sulphocyanate which contains two more molecules of ammonia than that discovered by Meitzendorf.* Our new substance was prepared by treating ten grams of cupric bromide with about fifteen cubic centimeters of strong ammoniac hydroxide, and

* Pogg. Annalen, LVI. 63, 92.

dissolving the resulting cupriammonium bromide by the addition of a little acetic acid. The addition to this mixture of a saturated solution of ammoniac sulphocyanate caused the precipitation of a blue basic compound, which was dissolved by addition of ammoniac hydrate. Soon deep blue crystals separated out from the solution. These were washed with alcohol and ether, and dried by pressing between filter paper. The washing with alcohol and ether must not be prolonged, otherwise the crystals lose their brilliant appearance and become covered with a coating of whitish basic salt. Prepared in this way, the compound occurs in very brilliant, deep blue crystals. On exposure to the air the crystals lose ammonia readily, and at the same time lose their brilliant lustre and become light blue in color. The salt is decomposed by water and by dilute acids; it is soluble in boiling concentrated hydrochloric acid, in cold strong nitric acid, and in ammoniac hydroxide.

Analyses of $\text{Cu}(\text{NH}_3)_4(\text{SCN})_2$.

- I. 0.2540 gram of substance gave, on electrolysis, 0.0641 gram of copper.
- II. 0.2064 gram of substance, distilled with caustic potash, required 33.71 cubic centimeters of a decinormal acid solution for neutralization.
- III. 0.3454 gram of substance, distilled with caustic potash, required 55.20 cubic centimeters of a decinormal acid solution for neutralization.
- IV. 0.1839 gram of substance required 14.71 cubic centimeters of a decinormal argentic nitrate solution to precipitate the sulphocyanic acid.
- V. 0.3555 gram of substance required 28.38 cubic centimeters of decinormal argentic nitrate solution for precipitation of sulphocyanic acid.

	Calculated for $\text{Cu}(\text{SCN})_2 \cdot 4\text{NH}_3$	Found.					
		I.	II.	III.	IV.	V.	Average.
Copper	25.63	25.23	. . .	. . .	. . .	. . .	25.23
Ammonia	27.52	. . .	27.81	27.26	. . .	. . .	27.54
Sulphocyanic acid	46.85	. . .	. . .	. . .	46.48	46.40	46.44
	100.00						99.21

The number of cuprammonium compounds, including the two classes *cupros-* and *cupri-*ammonium, seems to be almost unlimited. When a large amount of data has been accumulated, we shall be in a better position than we are at present to determine the constitution of these interesting bodies, and to explain their analogy to salts containing crystal water on the one hand, and their relations to the stable cobaltamine compounds on the other. For the present, the best that can be done is to multiply the available experimental evidence regarding them.

CAMBRIDGE, MASS., June, 1897.